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64271 Darmstadt

Liquid-crystalline medium

Liquid-crystalline medium

The invention relates to a liquid-crystalline medium, to twisted nematic (TN) and supertwisted nematic (STN) liquid-crystal displays having very short response times and good steepnesses and angle dependencies, and to the novel nematic liquid-crystal mixtures used therein.

TN displays are known, for example from M. Schadt and W. Helfrich, Appl. Phys. Lett., 18, 127 (1971). STN displays are known, for example from EP 0 131 216 B1; DE 34 23 993 A1; EP 0 098 070 A2; M. Schadt and F. Leenhouts, 17th Freiburg Congress on Liquid Crystals (8.-10.04.87); K. Kawasaki et al., SID 87 Digest 391 (20.6); M. Schadt and F. Leenhouts, SID 87 Digest 372 (20.1); K. Katoh et al., Japanese Journal of Applied Physics, Vol. 26, No. 11, L 1784-L 1786 (1987); F. Leenhouts et al., Appl. Phys. Lett. 50 (21), 1468 (1987); H.A. van Sprang and H.G. Koopman, J. Appl. Phys. 62 (5), 1734 (1987); T.J. Scheffer and J. Nehring, Appl. Phys. Lett. 45 (10), 1021 (1984), M. Schadt and F. Leenhouts, Appl. Phys. Lett. 50 (5), 236 (1987) and E.P. Raynes, Mol. Cryst. Liq. Cryst. Letters Vol. 4 (1), pp. 1-8 (1986). The term STN here covers any relatively highly twisted display element having a twist angle with a value of between 160° and 360°, such as, for example, the display elements according to Waters et al. (C.M. Waters et al., Proc. Soc. Inf. Disp. (New York) (1985) (3rd Intern. Display Conference, Kobe, Japan), STN-LCDs (DE-A 35 03 259), SBE-LCDs (T.J. Scheffer and J. Nehring, Appl. Phys. Lett. 45 (1984) 1021), OMI-LCDs (M. Schadt and F. Leenhouts, Appl. Phys. Lett. 50 (1987), 236, DST-LCDs (EP-A 0 246 842) or BW-STN-LCDs (K. Kawasaki et al., SID 87 Digest 391 (20.6)).

In particular, STN displays are distinguished compared with standard TN displays by significantly better steepnesses of the electro-optical characteristic line and, associated therewith, better contrast values, and by significantly lower angle dependence of the contrast.

Of particular interest are TN and STN displays having very short response times, in particular also at relatively low temperatures. In order to achieve short response times, the rotational viscosities of the liquid-crystal mixtures

have hitherto been optimised using mostly monotropic additives having relatively high vapour pressure. However, the response times achieved were not adequate for every application.

In order to achieve a steep electro-optical characteristic line in the displays according to the invention, the liquid-crystal mixtures should have relatively large values for the ratio between the elastic constants K_{33}/K_{11} and relatively small values for $\Delta\varepsilon/\varepsilon_{\perp}$, where $\Delta\varepsilon$ is the dielectric anisotropy and $\varepsilon_{\perp}$ is the dielectric constant perpendicular to the longitudinal molecular axis.

In addition to optimisation of the contrast and response times, further important requirements are made of mixtures of this type:

1. broad d/p window
2. high long-term chemical stability
3. high electrical resistance
4. low frequency and temperature dependence of the threshold voltage.

The parameter combinations achieved are still far from adequate, in particular for high-multiplex STN displays (with a multiplex rate in the region of about 1/400), but also for medium- and low-multiplex STN displays (with multiplex rates in the region of about 1/64 and 1/16 respectively), and TN displays. This is partly attributable to the fact that the various requirements are affected in opposite manners by material parameters.

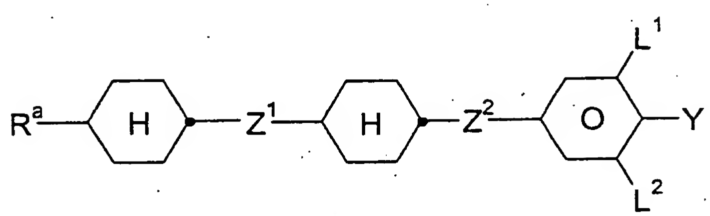
A requirement for display applications of relatively low resolution (mux 1/16) is an operating voltage in the region around 3 V at birefringence values of Δn = 0.13-0.14. To this end, liquid-crystal mixtures having threshold voltages of less than 1 V and typically in the range V_{10} = 0.65-0.75 V must be provided. Liquid-crystal mixtures from the prior art comprising highly polar substances containing a nitrile group, which are already employed up to the solubility limit, generally do not achieve the requisite combination of low threshold voltage and low birefringence.

Thus, there continues to be a great demand for TN and STN displays, in particular for medium- and low-multiplex STN displays, having very short response times at the same time as a large working-temperature range, high characteristic-line steepness, good angle dependence of the contrast and low threshold voltage which meet the above-mentioned requirements.

The object of the present invention is to provide mixtures having a low threshold voltage and low birefringence, in particular for TN and STN applications, which comprise compounds which are distinguished by low birefringence and moderate polarity.

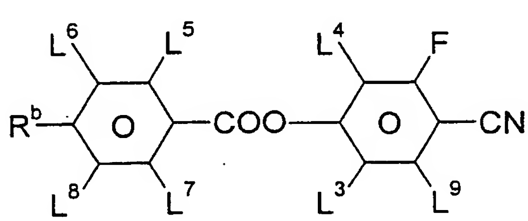
The invention furthermore has the object of providing liquid-crystalline media, in particular for TN and STN displays, which do not have the above-mentioned disadvantages or only do so to a lesser extent and at the same time have short response times, in particular at low temperatures, and very good steepnesses.

It has now been found that this object can be achieved if use is made of liquid-crystal mixtures which comprise one or more compounds of the formula A



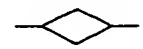
A

and at least one compound of the formula B



B

in which

R^a and R^b are each, independently of one another, H or an alkyl radical having from 1 to 12 carbon atoms which is unsubstituted, monosubstituted by CN or CF_3 or at least monosubstituted by halogen, where one or more CH_2 groups in these radicals may also each, independently of one another, be replaced by -O-, -S-,  , -CH=CH-, -C≡C-, -CO-, -CO-O-, -O-CO- or -O-CO-O- in such a way that O atoms are not linked directly to one another,

Z^1 and Z^2 are each, independently of one another, $-(CH_2)_4-$, $-CF_2O-$, -COO-, $-OCF_2-$, $-OCH_2-$, $-CH_2O-$, $-CH_2-$, $-(CH_2)_3-$ or a single bond, in which at least one bridge is $-OCF_2-$ or $-CF_2O-$,

L^1 to L^9 are each, independently of one another, H or F, and

Y is F, Cl, SF_5, NCS, SCN, CN, OCN, or a monohalogenated or polyhalogenated alkyl, alkoxy, alkenyl or alkenyloxy radical, each having up to 5 carbon atoms.

The use of substances of the formula A which have moderate polarity and low birefringence gives TN and STN media which are distinguished by low threshold voltages and low Δn values.

The use of the compounds of the formulae A and B in the mixtures for TN and STN displays according to the invention results in

- high steepness of the electro-optical characteristic line,
- low temperature dependence of the threshold voltage, and
- very fast response times, in particular at low temperatures.

The compounds of the formulae A and B significantly shorten, in particular, the response times of TN and STN mixtures while simultaneously

increasing the steepness and reducing the temperature dependence of the threshold voltage.

The mixtures according to the invention are furthermore distinguished by the following advantages:

- they have low viscosity,
- they have a low threshold voltage and operating voltage, and
- they effect long shelf lives in the display at low temperatures.

The invention furthermore relates to a liquid-crystal display having

- two outer plates, which, together with a frame, form a cell,
- a nematic liquid-crystal mixture of positive dielectric anisotropy located in the cell,
- electrode layers with alignment layers on the insides of the outer plates,
- a tilt angle between the longitudinal axis of the molecules at the surface of the outer plates and the outer plates of from 0 degree to 30 degrees, and
- a twist angle of the liquid-crystal mixture in the cell from alignment layer to alignment layer with a value of between 22.5° and 600°,
- a nematic liquid-crystal mixture consisting of

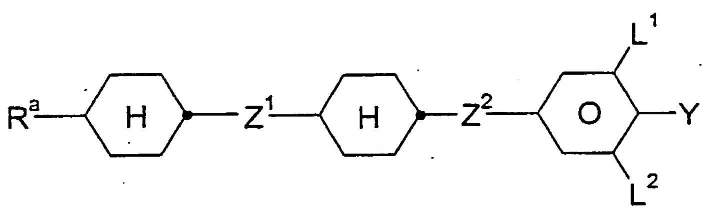
    a) 15 – 75% by weight of a liquid-crystalline <u>component A</u> consisting of one or more compounds having a dielectric anisotropy of greater than +1.5;

    b) 25 – 85% by weight of a liquid-crystalline <u>component B</u> consisting of one or more compounds having a dielectric anisotropy of between -1.5 and +1.5;

    c) 0 – 20% by weight of a liquid-crystalline <u>component D</u> consisting of one or more compounds having a dielectric anisotropy of below -1.5, and

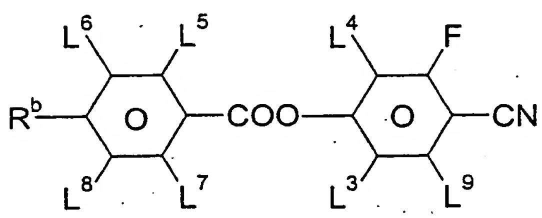
d) if desired, an optically active <u>component C</u> in such an amount that the ratio between the layer thickness (separation of the outer plates) and the natural pitch of the chiral nematic liquid-crystal mixture is from about 0.2 to 1.3,

characterised in that <u>component A</u> comprises at least one compound of the formula A



A

and at least one compound of the formula B

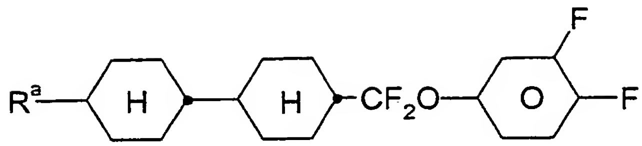


B

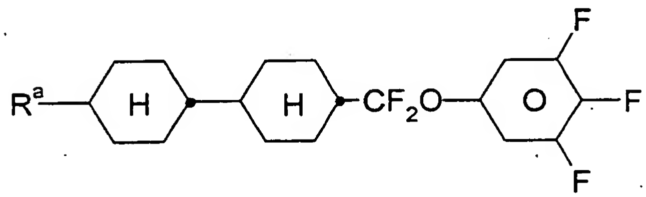
in which R^a, R^b, Z^1, Z^2, L^1, L^2, L^3, L^4, L^5, L^6, L^7, L^8, L^9 and Y are as defined above.

The invention also relates to TN and STN displays, in particular medium- and low-multiplexed STN displays, which contain the liquid-crystal mixture according to the invention. The mixtures according to the invention are furthermore used in IPS mixtures.

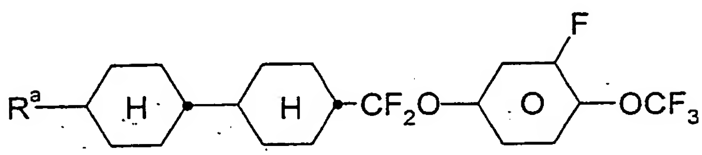
Formula A covers, in particular, compounds of the sub-formulae A-1 to A-12



A-1



A-2



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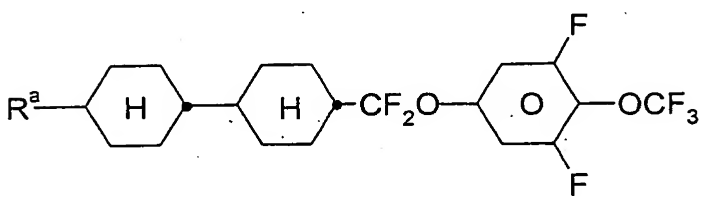

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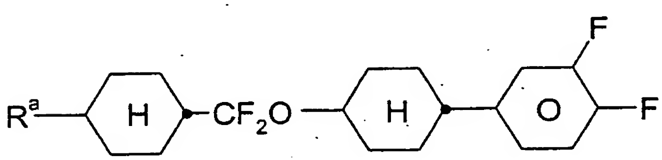

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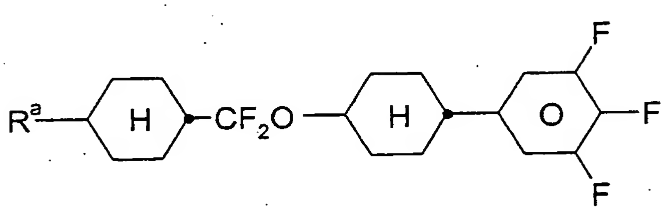
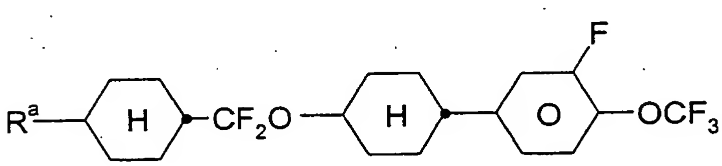
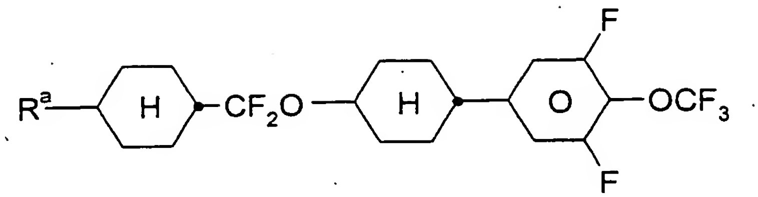


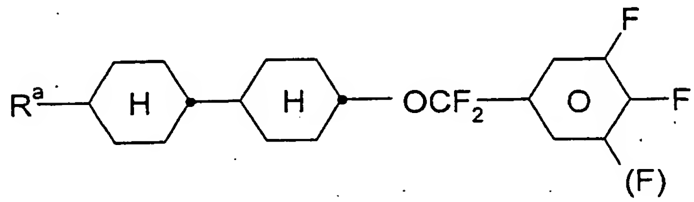
A-6



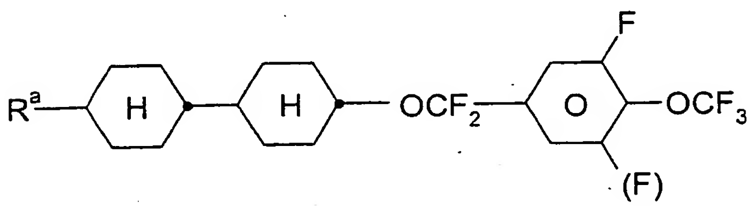
A-7



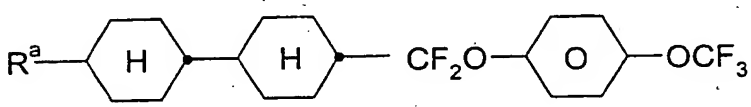
A-8



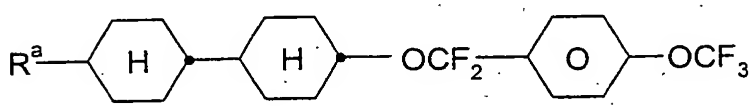
A-9



A-10



A-11



A-12

in which R^a is as defined in Claim 1.

Particular preference is given to mixtures according to the invention which comprise at least one compound of the formula A-2 and/or A-6.

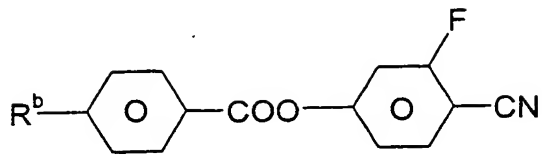
In the formulae A and A-1 to A-12, R^a is particularly preferably straight-chain alkyl or alkoxy, 1E-alkenyl or 3E-alkenyl having from 2 to 7 carbon atoms.

Z^1 is preferably a single bond, and Z^2 is preferably $-CF_2O-$. L^1 and L^2 are preferably F.

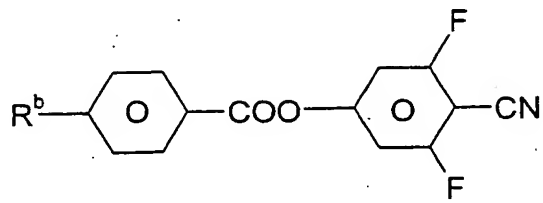
Y is preferably F, Cl, CN, CF_3, C_2F_5, C_3F_7, CF_2H, OCF_3, OCF_2H, $OCFHCF_3$, $OCFHCFH_2$, $OCFHCF_2H$, OCF_2CH_3, OCF_2CFH_2, OCF_2CF_2H,

$OCF_2CF_2CF_2H$, $OCF_2CF_2CFH_2$, $OCFHCF_2CF_3$, $OCFHCF_2CF_2H$, $OCFHCFHCF_3$, $OCH_2CF_2CF_3$, $OCF_2CF_2CF_3$, $OCF_2CFHCFH_2$, $OCF_2CH_2CF_2H$, $OCFHCF_2CFH_2$, $OCFHCFHCF_2H$, $OCFHCH_2CF_3$, OCH_2CFHCF_3, $OCH_2CF_2CF_2H$, OCF_2CFHCH_3, $OCF_2CH_2CFH_2$, $OCFHCF_2CH_3$, $OCFHCFHCFH_2$, $OCFHCH_2CF_3$, $OCH_2CF_2CFH_2$, OCH_2CFHCF_2H, $OCF_2CH_2CH_3$, $OCFHCFHCH_3$, $OCFHCH_2CFH_2$, $OCH_2CF_2CH_3$, $OCH_2CFHCFH_2$, $OCH_2CH_2CF_2H$, $OCHCH_2CH_3$, OCH_2CFHCH_3, $OCH_2CH_2CF_2H$, $OCClFCF_3$, $OCClFCClF_2$, $OCClFCFH_2$, $OCFHCCl_2F$, $OCClFCF_2H$, $OCClFCClF_2$, OCF_2CClH_2, OCF_2CCl_2H, OCF_2CCl_2F, OCF_2CClFH, OCF_2CClF_2, $OCF_2CF_2CClF_2$, $OCF_2CF_2CCl_2F$, $OCClFCF_2CF_3$, $OCClFCF_2CF_2H$, $OCClFCF_2CClF_2$, $OCClFCFHCF_3$, $OCClFCClFCF_3$, $OCCl_2CF_2CF_3$, $OCClHCF_2CF_3$, $OCClFCF_2CF_3$, $OCClFCClFCF_3$, $OCF_2CClFCFH_2$, $OCF_2CF_2CCl_2F$, $OCF_2CCl_2CF_2H$, $OCF_2CH_2CClF_2$, $OCClFCF_2CFH_2$, $OCFHCF_2CCl_2F$, $OCClFCFHCF_2H$, $OCClFCClFCF_2H$, $OCFHCFHCClF_2$, $OCClFCH_2CF_3$, $OCFHCCl_2CF_3$, $OCCl_2CFHCF_3$, $OCH_2CClFCF_3$, $OCCl_2CF_2CF_2H$, $OCH_2CF_2CClF_2$, $OCF_2CClFCH_3$, $OCF_2CFHCCl_2H$, $OCF_2CCl_2CFH_2$, $OCF_2CH_2CCl_2F$, $OCClFCF_2CH_3$, $OCFHCF_2CCl_2H$, $OCClFCClFCFH_2$, $OCFHCFHCCl_2F$, $OCClFCH_2CF_3$, $OCFHCCl_2CF_3$, $OCCl_2CF_2CFH_2$, $OCH_2CF_2CCl_2F$, $OCCl_2CFHCF_2H$, $OCClHCClFCF_2H$, $OCF_2CClHCClH_2$, $OCF_2CH_2CCl_2H$, $OCClFCFHCH_3$, $OCF_2CClFCCl_2H$, $OCClFCH_2CFH_2$, $OCFHCCl_2CFH_2$, $OCCl_2CF_2CH_3$, $OCH_2CF_2CClH_2$, $OCCl_2CFHCFH_2$, $OCH_2CClFCFCl_2$, $OCH_2CH_2CF_2H$, $OCClHCClHCF_2H$, $OCH_2CCl_2CF_2H$, $OCClFCH_2CH_3$, $OCFHCH_2CCl_2H$, $OCClHCFHCClH_2$, $OCH_2CFHCCl_2H$, $OCCl_2CH_2CF_2H$, $OCH_2CCl_2CF_2H$, $CH=CF_2$, $CF=CF_2$, $OCH=CF_2$, $OCF=CF_2$, $CH=CHF$, $OCH=CHF$, $CF=CHF$ or $OCF=CHF$, in particular F, Cl, CN, CF_3, CF_2H, C_2F_5, C_3F_7, OCF_3, OCF_2H, $OCFHCF_3$, $OCFHCFH_2$, $OCFHCF_2H$, OCF_2CH_3, OCF_2CFH_2, OCF_2CF_2H, $OCF_2CF_2CF_2H$, $OCF_2CF_2CFH_2$, $OCFHCF_2CF_3$, $OCFHCF_2CF_2H$, $OCF_2CF_2CF_3$, OCF_2CHFCF_3 or $OCClFCF_2CF_3$.

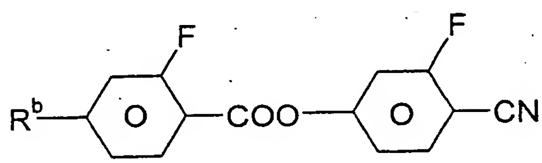
Formula B covers, in particular, compounds of the sub-formulae B-1 to B-6



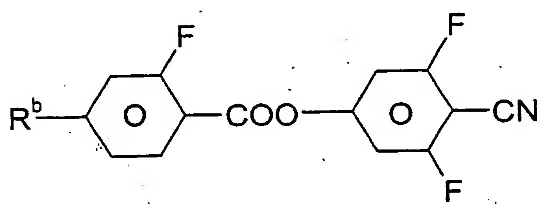
B-1



B-2



B-3



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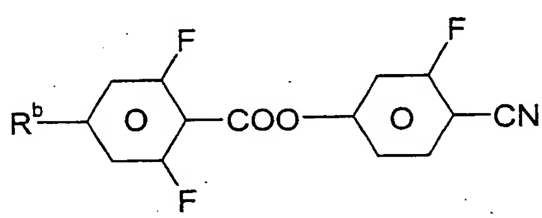
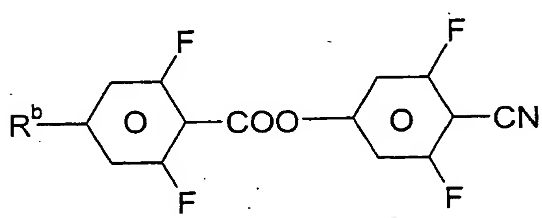


B-5



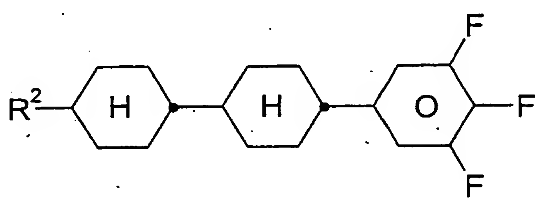
B-6

in which R^b is as defined in Claim 1.

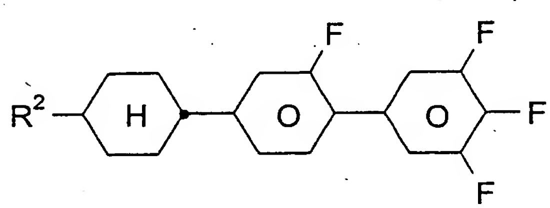
Particular preference is given to compounds in which R^b is a straight-chain alkyl radical having 1-7 carbon atoms or an alkenyl radical having 2-7 carbon atoms. Especial preference is given to compounds of the formulae B-1, B-2 and B-4.

The use of compounds of the formulae A and B in the liquid-crystal mixtures according to the invention results in particularly low rotational viscosity values and in TN and STN displays having high steepness and fast response times, in particular at low temperatures.

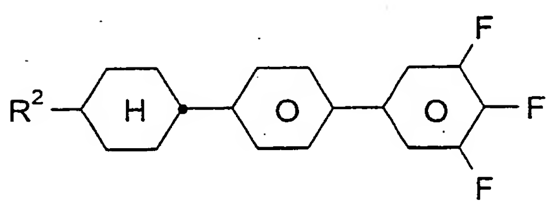
Besides the compounds of the formula A, component A or the liquid-crystalline mixture according to the invention preferably additionally comprises one or more 3,4,5-trifluorophenyl compounds selected from the group consisting of the compounds of the formulae IIa to IIj



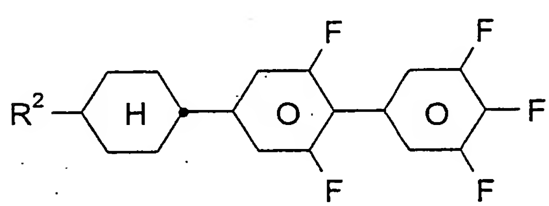
IIa



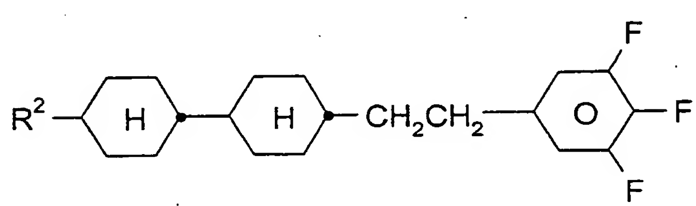
IIb



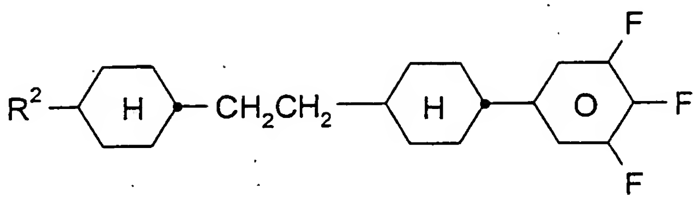
IIc



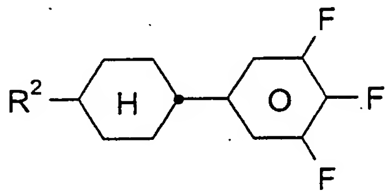
IId



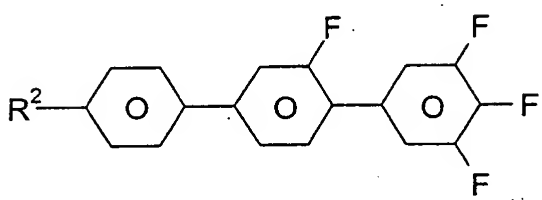
IIe



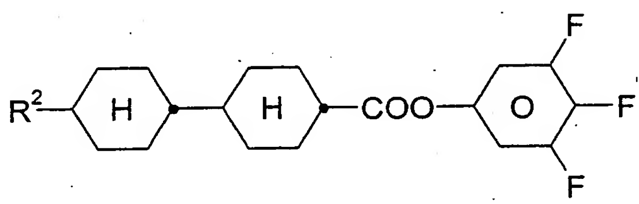
IIf



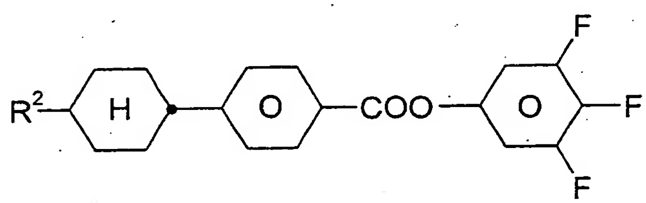
IIg



IIh

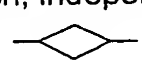


IIi

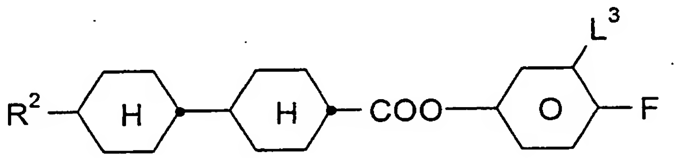


IIj

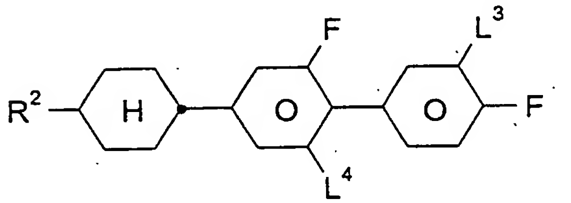
in which

R^2 is H or an alkyl radical having from 1 to 12 carbon atoms which is unsubstituted, monosubstituted by CN or CF_3 or at least monosubstituted by halogen, where one or more CH_2 groups in these radicals may also each, independently of one another, be replaced by -O-, -S-,  , -CH=CH-, -C≡C-, -CO-, -CO-O-, -O-CO- or -O-CO-O- in such a way that O atoms are not linked directly to one another.

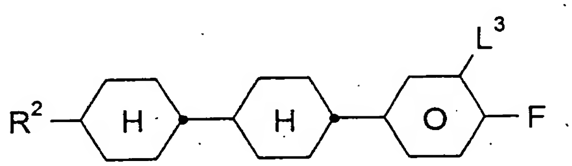
Besides the compounds of the formulae A and B, the medium according to the invention may additionally comprise one or more compounds containing a polar end group, of the formulae II*a to II*s



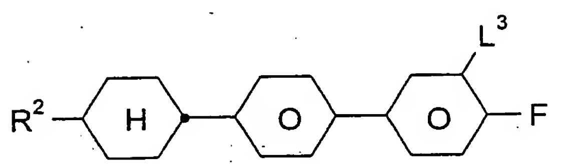
II*a



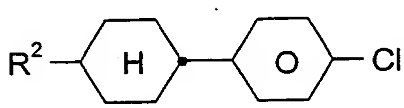
II*b



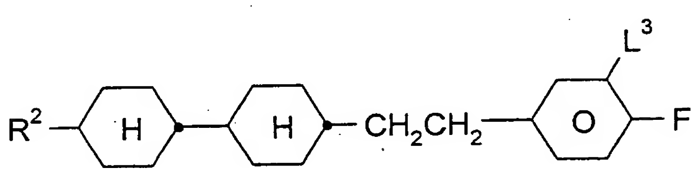
II*c



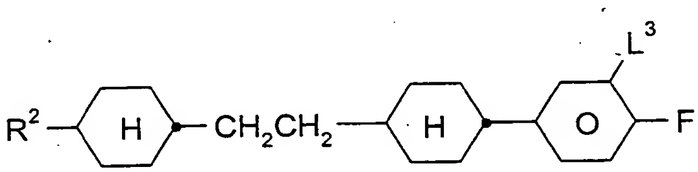
II*d



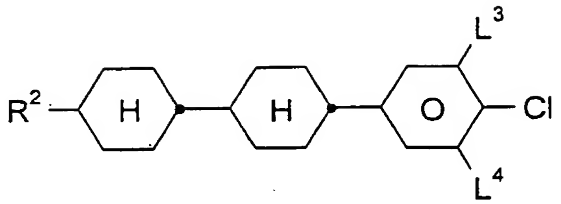
II*e



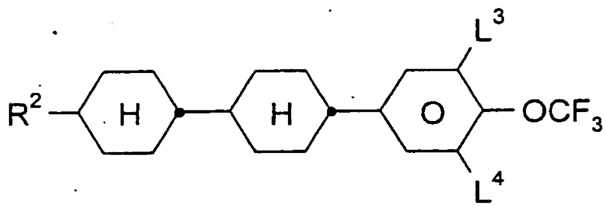
II*f



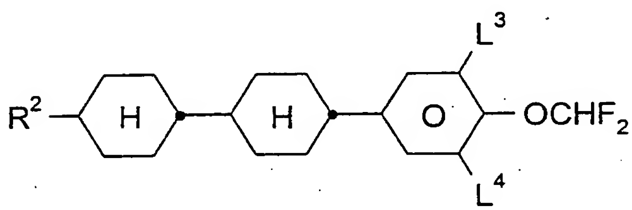
II*g



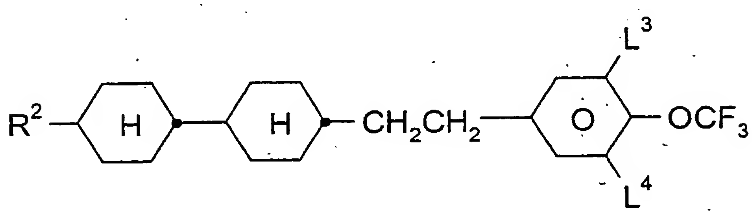
II*h



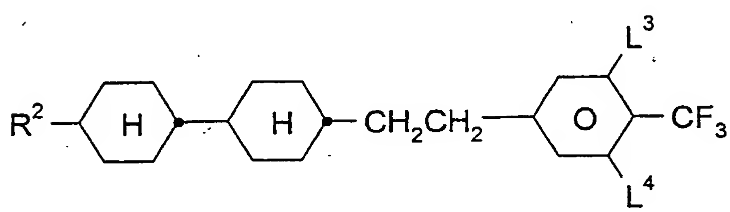
II*i



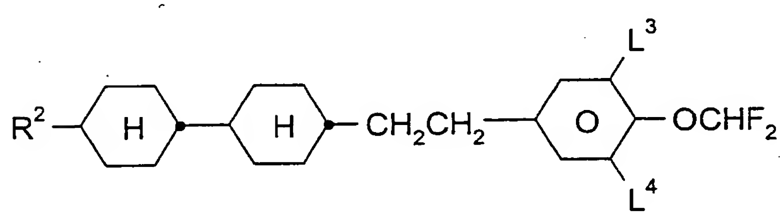
II*k



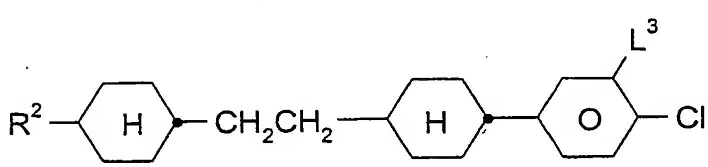
II*m



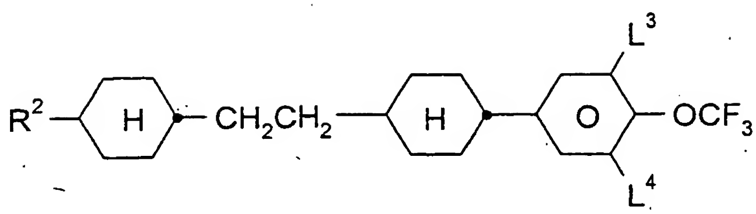
II*n



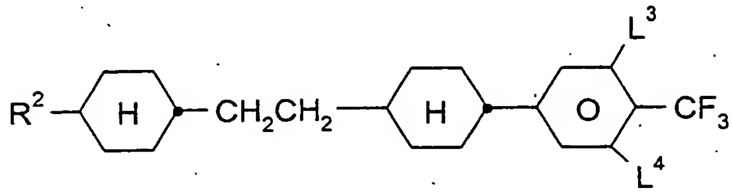
II*o



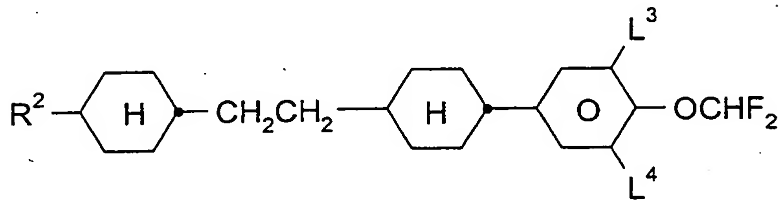
II*p



II*q



II*r

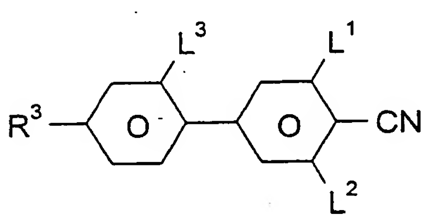


II*s

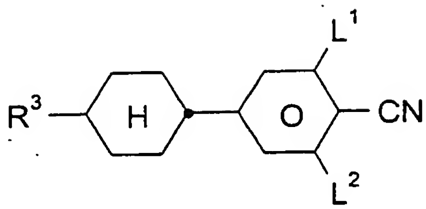
in which R^2 is as defined for R^a, and L^3 and L^4 are each, independently of one another, H or F. R^2 in these compounds is particularly preferably alkyl, alkenyl or alkoxy having up to 7 carbon atoms.

The medium according to the invention or component A particularly preferably comprises compounds of the formulae IIa, IIb, IIc, IId, IIe, IIf, IIg, IIj, II*b, II*c, II*d, II*f and/or II*i, in particular compounds of the formulae IIa, IIb, IId, IIi, II*a and II*i.

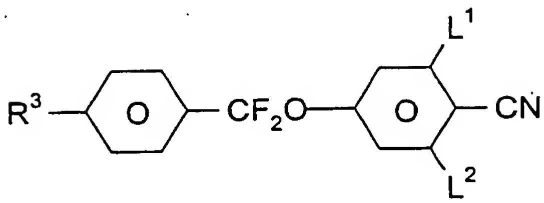
Besides one or more compounds of the formula B, the mixture according to the invention preferably comprises one or more cyano compounds of the formulae IIIa to IIIi:



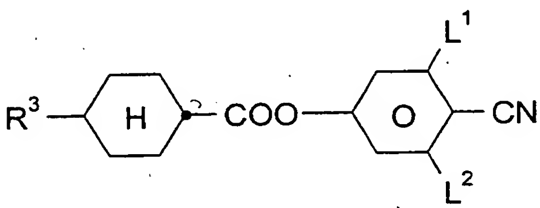
IIIa



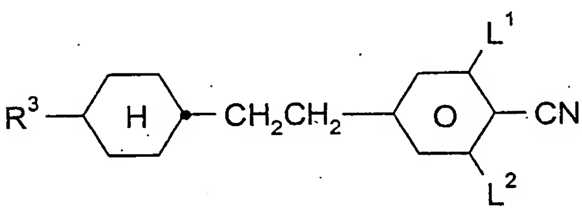
IIIb



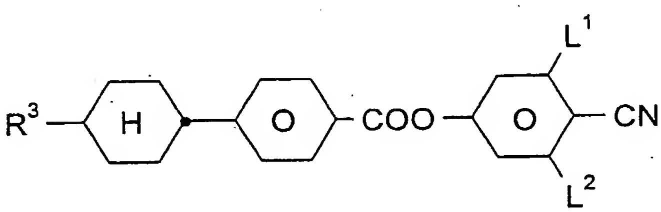
IIIc



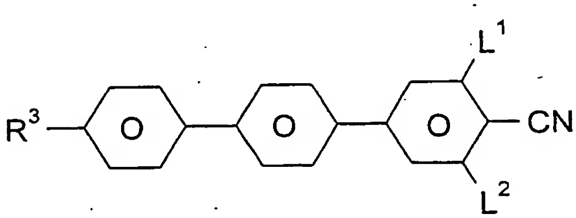
IIId



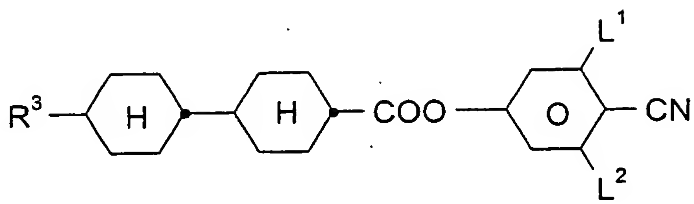
IIIe



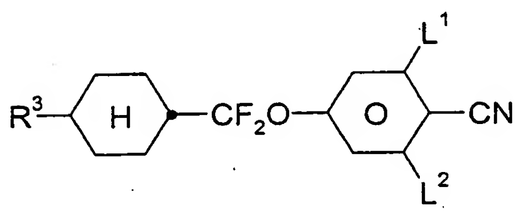
IIIf



IIIg



IIIh



IIIi

in which R^3 is as defined for R^a, and L^1, L^2 and L^3 are each, independently of one another, H or F. R^3 in these compounds is particularly preferably alkyl, alkenyl or alkoxy having up to 7 carbon atoms.

Particular preference is given to mixtures which comprise one or more compounds of the formulae IIIb, IIIc and IIIf, in particular those in which L^1 and/or L^2 is F.

Preference is furthermore given to mixtures which comprise one or more compounds of the formula IIIf and/or IIIg in which L^2 is H and L^1 is H or F, in particular F.

The individual compounds of the formulae A, B and of the formulae IIa-IIj, II*a-II*s and IIIa to IIIi and their sub-formulae or also other compounds which can be used in the mixtures or TN and STN displays according to the invention are either known or can be prepared analogously to the known compounds.

The compounds of the formula A have low viscosities, in particular low rotational viscosities, and low values for the ratio between the elastic constants K_{33}/K_{11}, and therefore result in short response times in the displays according to the invention, while the presence of compounds of the formula B of high dielectric anisotropy, in particular in increased concentrations, causes a reduction in the viscosity.

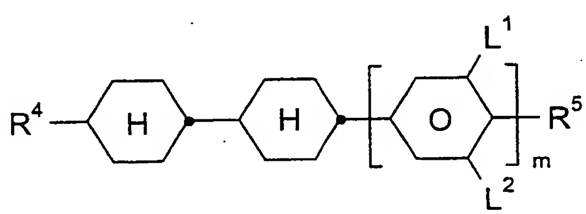
Preferred liquid-crystal mixtures comprise one or more compounds of component A, preferably in a proportion of from 15% to 75%, particularly preferably from 20% to 65%. These compounds have a dielectric anisotropy of $\Delta\varepsilon \geq +3$, in particular of $\Delta\varepsilon \geq +8$, particularly preferably of $\Delta\varepsilon \geq +12$.

Further preferred mixtures comprise

- one or more, in particular from two to four, compounds of the formula A,
- in each case one, two or three compounds of the formula A-2,
- one or more, in particular one or two, compounds of the formula B,
- one or more, in particular from two to five, compounds of the formulae IIIa, IIIb, IIIc and/or IIIf.

Preferred liquid-crystal mixtures comprise one or more compounds of component B, preferably from 25 to 85%. The compounds from group B are distinguished, in particular, by their low values for the rotational viscosity γ_1.

Component B preferably comprises one or more compounds of the formula IV



IV

in which

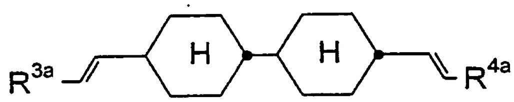
m is 0 or 1,

R^4 is an alkenyl group having from 2 to 7 carbon atoms,

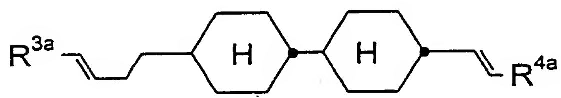
R^5 is as defined for R^a or, if m = 1, is alternatively F, Cl, CF_3 or OCF_3,

L^1 and L^2 are each, independently of one another, H or F.

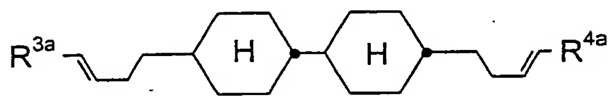
Particularly preferred compounds of the formula IV are those in which R^4 is alkenyl having from 2 to 7 carbon atoms, in particular those of the following formulae:



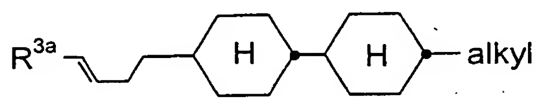
IV-1



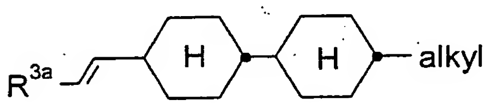
IV-2



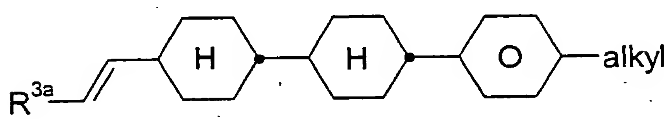
IV-3



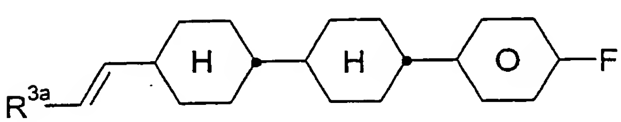
IV-4



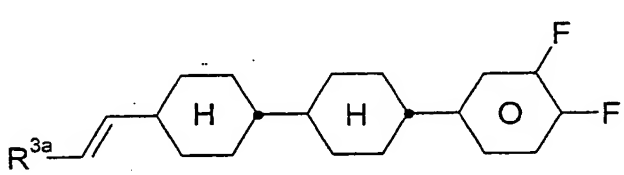
IV-5



IV-6



IV-7



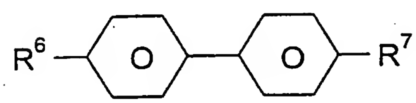
IV-8

in which R^{3a} and R^{4a} are each, independently of one another, H, CH_3, C_2H_5 or n-C_3H_7, and alkyl is an alkyl group having from 1 to 7 carbon atoms.

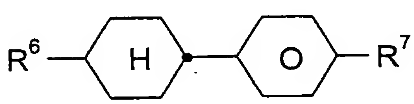
Particular preference is given to TN and STN displays according to the invention in which the liquid-crystal mixture comprises at least one compound of the formula IV-1 and/or IV-3 in which R^{3a} and R^{4a} each have the same meaning, and displays in which the liquid-crystal mixture comprises at least one compound of the formula IV-5.

In a further preferred embodiment, the mixtures according to the invention comprise one or more compounds of the formula IV-6.

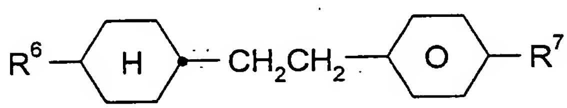
Component B preferably furthermore comprises compounds selected from the group consisting of the bicyclic compounds of the formulae V-1 to V-9



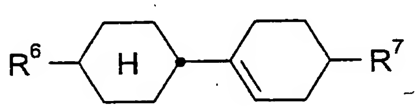
V-1



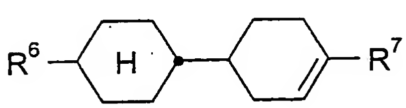
V-2



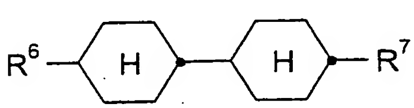
V-3



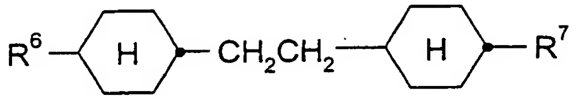
V-4



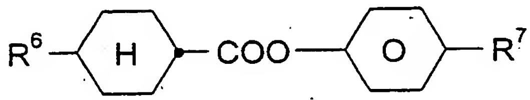
V-5



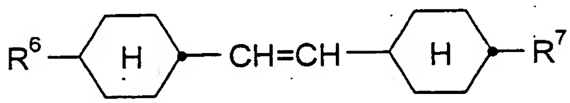
V-6



V-7

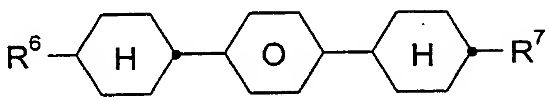


V-8

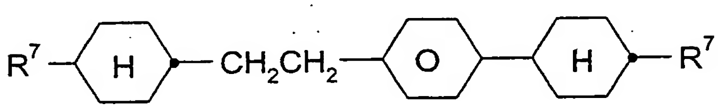


V-9

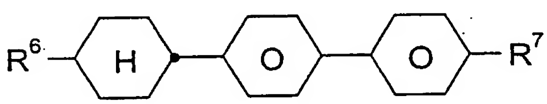
and/or one or more compounds selected from the group consisting of the tricyclic compounds of the formulae V-10 to V-27



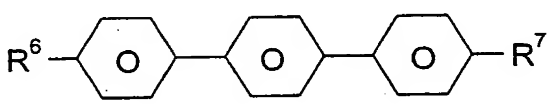
V-10



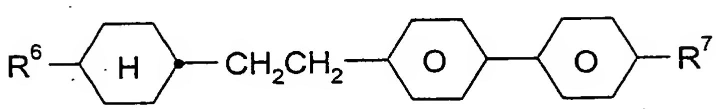
V-11



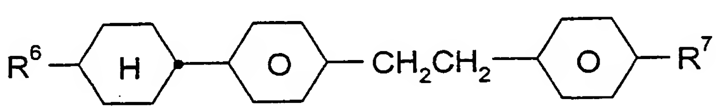
V-12



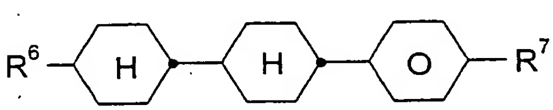
V-13



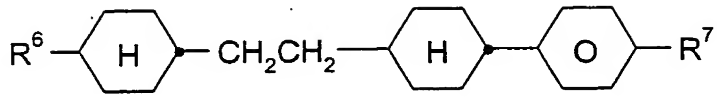
V-14



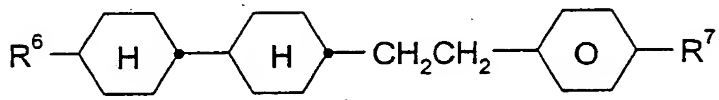
V-15



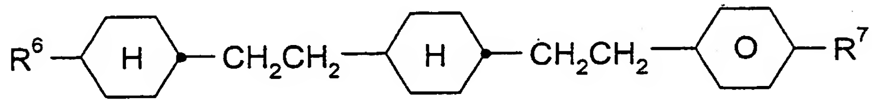
V-16



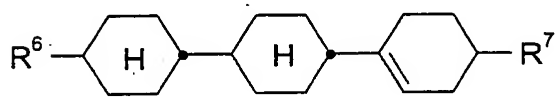
V-17



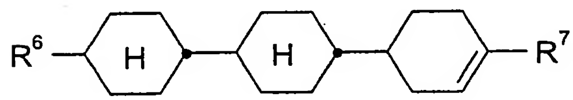
V-18



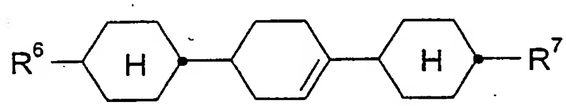
V-19



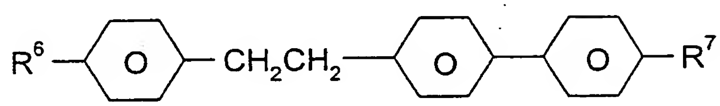
V-20



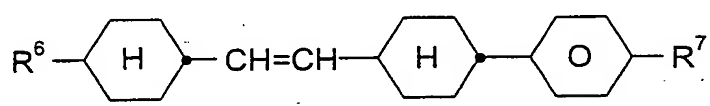
V-21



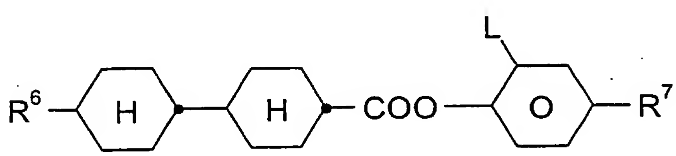
V-22



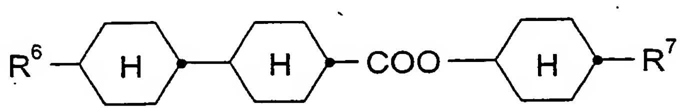
V-23



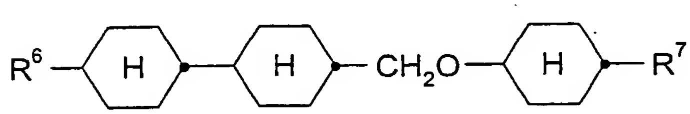
V-24



V-25

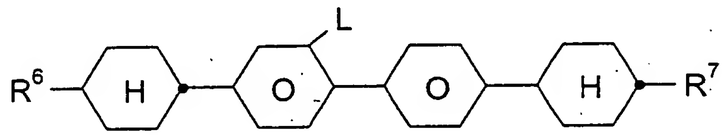


V-26

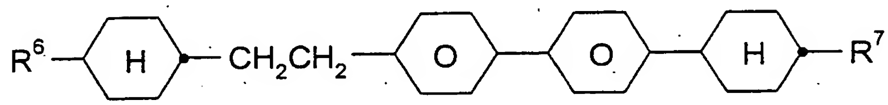


V-27

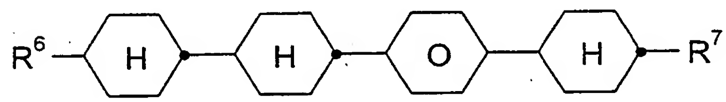
and/or one or more compounds selected from the group consisting of the tetracyclic compounds of the formulae V-28 to V-34



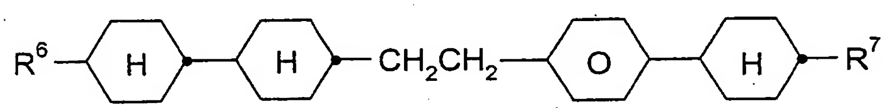
V-28



V-29



V-30



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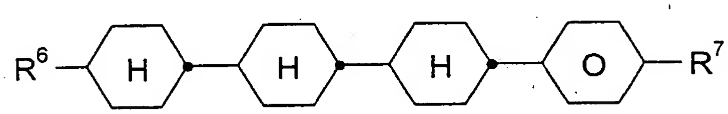
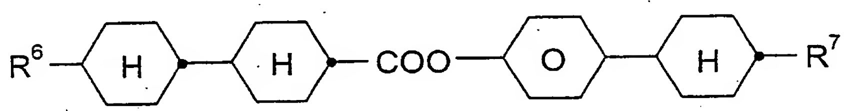
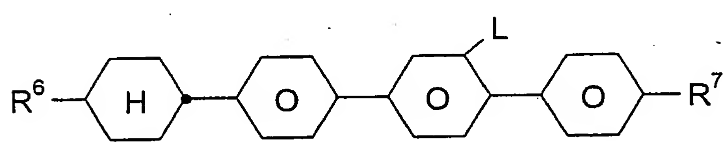


V-32



V-33



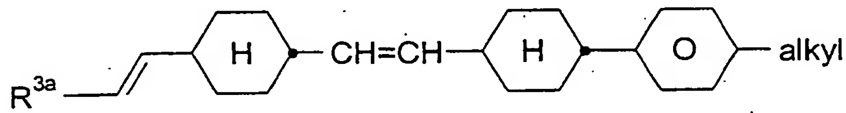
V-34

in which R^6 and R^7 are as defined for R^a in Claim 1, and L is H or F.

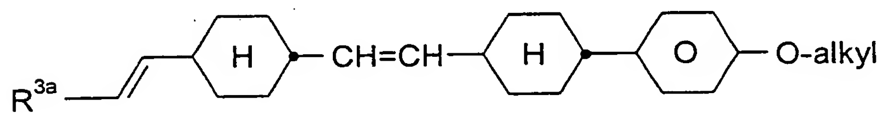
Particular preference is given to compounds of the formulae V-25 to V-34 in which R^6 is alkyl and R^7 is alkyl or alkoxy, in particular alkoxy, each having from 1 to 7 carbon atoms. Preference is furthermore given to compounds of the formulae V-25, V-28 and V-34 in which L is F.

R^6 and R^7 in the compounds of the formulae V-1 to V-34 are particularly preferably straight-chain alkyl or alkoxy having from 1 to 12 carbon atoms.

Particular preference is given to mixtures according to the invention which comprise one or more compounds of the formula B-3a and/or B-5a



B-3a



B-5a

The mixtures preferably comprise 2-25% by weight, in particular 2-15% by weight, of compounds of the formula B-5a.

If desired, the liquid-crystalline mixtures comprise an optically active <u>component C</u> in such an amount that the ratio between the layer thickness (separation of the outer plates) and the natural pitch of the chiral nematic liquid-crystal mixture is greater than 0.2. A multiplicity of chiral dopants, some of which are commercially available, is available to the person skilled in the art for the component, such as, for example, cholesteryl nonanoate, S-811, S-1011 and S-2011 from Merck KGaA, Darmstadt, and CB15 (BDH, Poole, UK). The choice of dopants is not crucial per se.

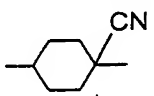
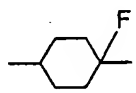
The proportion of the compounds of component C is preferably from 0 to 10%, in particular from 0 to 5%, particularly preferably from 0 to 3%.

The mixtures according to the invention may also, if desired, comprise up to 20% of one or more compounds having a dielectric anisotropy of less than -1,5 (<u>component D</u>).

If the mixtures comprise compounds of <u>component D</u>, these are preferably one or more compounds containing the structural unit 2,3-difluoro-1,4-phenylene, for example compounds as described in DE-A 38 07 801,

38 07 861, 38 07 863, 38 07 864 or 38 07 908. Particular preference is given to tolans containing this structural unit, as described in International Patent Application PCT/DE 88/00133.

Further known compounds of component D are, for example, derivatives of 2,3-dicyanohydroquinones or cyclohexane derivatives containing the structural unit

 or  , as described in DE-A 32 31 707 and DE-A 34 07 013.

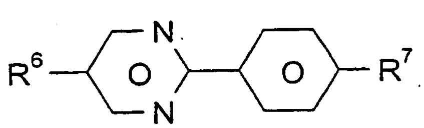
The liquid-crystal displays according to the invention preferably contain no compounds of <u>component D</u>.

The term "alkenyl" in the definition of R^a, R^b, R^2, R^3, R^4, R^5, R^6 and R^7 covers straight-chain and branched alkenyl groups, in particular the straight-chain groups. Particularly preferred alkenyl groups are C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl, C_5-C_7-4-alkenyl, C_6-C_7-5-alkenyl and C_7-6-alkenyl, in particular C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl and C_5-C_7-4-alkenyl.

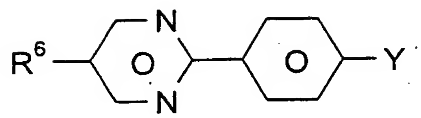
Examples of preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 carbon atoms are generally preferred.

Further preferred embodiments relate to liquid-crystal mixtures according to the invention which

- additionally comprise one or more, particularly preferably one, two or three, heterocyclic compounds of the formula Va and/or Vb



Va



Vb

in which

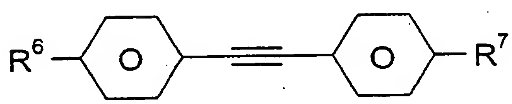
R^6 and R^7 are as defined above,

and

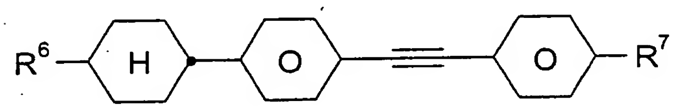
Y is F, Cl or OCF_3,

- the proportion of the compounds from the group consisting of Va and Vb is preferably from 2 to 35%, in particular from 5 to 20%,

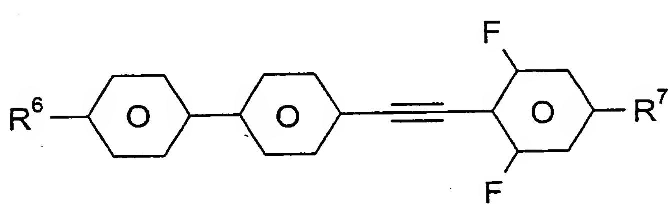
additionally comprise one or more, particularly preferably one, two or three, tolan compounds of the formulae T2a, T2b and/or T2c



T2a



T2b



T2c

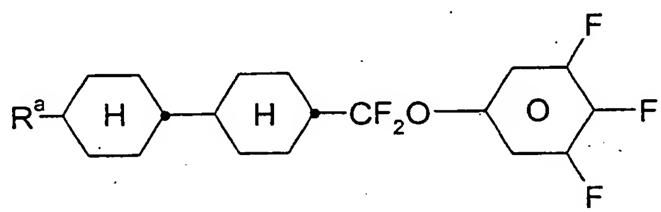
in which R^6 and R^7 are as defined above.

The proportion of the compounds from the group consisting of T2a, T2b and/or T2c is preferably from 2 to 20%, in particular from 4 to 12%. The

mixture according to the invention preferably comprises two or three compounds of the formula T2a and/or T2b.

In particularly preferred embodiments, the mixtures comprise

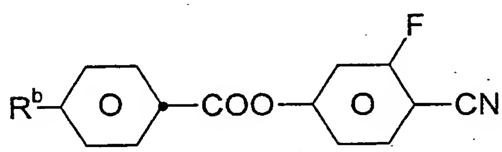
- at least one compound of the formula A-2



A-2

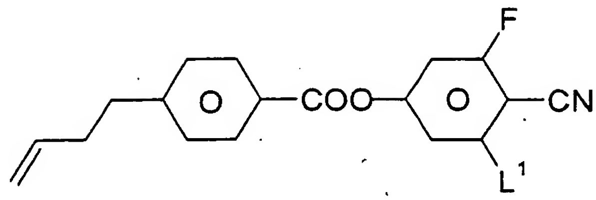
and

at least one compound of the formula B-1



B-1

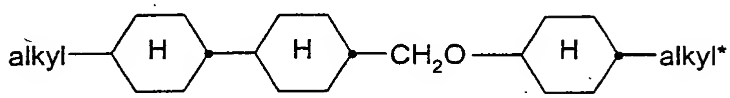
- at least one compound of the formula IIj;
- at least one tolan compound of the formula T2c;
- at least two, in particular three, compounds of the formula A;
- at least two, in particular three, compounds of the formula B;
- at least one compound of the formula T2a and at least one compound of the formula T2b;
- at least one compound of the formula VI



VI

in which L^1 is H or F;

- at least one compound of the formula VII



VII

in which alkyl and alkyl* are each, independently of one another, an alkyl group having from 1 to 7 carbon atoms;

- at least from 2 to 30% by weight, preferably 2 – 25% by weight, in particular from 3 to 15% by weight, of compounds of the formula VII;

- at least 2.5% by weight of the compounds of the formula IV-5;

- 5-30% by weight, preferably 10-25% by weight, of the compounds of the formula A;

- 5-30% by weight, preferably 5-20% by weight, of the compounds of the formula B;

- at least three homologues of the compounds of the formula A, where R^a is then preferably C_2H_5, n-C_3H_7 or n-C_5H_{11}.

Further particularly preferred embodiments relate to liquid-crystal mixtures which comprise

- a total of from three to six compounds of the formulae A and B, where the proportion of these compounds with respect to the mixture as a whole is from 25 to 65%, in particular from 30 to 55%,

- more than 20% of compounds of positive dielectric anisotropy, in particular having $\Delta\varepsilon \geq +12$.

The mixtures according to the invention are distinguished, in particular on use in TN and STN displays of high layer thicknesses, by very low total response times ($t_{tot} = t_{on} + t_{off}$).

The liquid-crystal mixtures used in the TN and STN cells according to the invention are dielectrically positive, with $\Delta\varepsilon \geq 1$. Particular preference is given to liquid-crystal mixtures with $\Delta\varepsilon \geq 3$, in particular with $\Delta\varepsilon \geq 5$.

The liquid-crystal mixtures according to the invention have favourable values for the threshold voltage $V_{10/0/20}$ and for the rotational viscosity γ_1. If the value for the optical path difference $d \cdot \Delta n$ is pre-specified, the value for the layer thickness d is determined by the optical anisotropy Δn. In particular at relatively high values for $d \cdot \Delta n$, the use of liquid-crystal mixtures according to the invention having a relatively high value for the optical anisotropy is generally preferred, since the value for d can then be selected to be relatively small, which results in more favourable values for the response times. However, liquid-crystal displays according to the invention which contain liquid-crystal mixtures according to the invention with smaller values for Δn are also characterised by advantageous values for the response times.

The liquid-crystal mixtures according to the invention are furthermore characterised by advantageous values for the steepness of the electro-optical characteristic line, and can be operated with high multiplex rates, in particular at temperatures above 20°C. In addition, the liquid-crystal mixtures according to the invention have high stability and favourable values for the electrical resistance and the frequency dependence of the threshold voltage. The liquid-crystal displays according to the invention have a large working-temperature range and good angle dependence of the contrast.

The construction of the liquid-crystal display elements according to the invention from polarisers, electrode base plates and electrodes having a surface treatment such that the preferential alignment (director) of the

liquid-crystal molecules in each case adjacent thereto is usually twisted by a value of from 160° to 720° from one electrode to the other corresponds to the usual structure for display elements of this type. The term "usual structure" here is broadly drawn and also covers all derivatives and modifications of the TN and STN cell, in particular also matrix display elements and display elements containing additional magnets.

The surface tilt angle at the two outer plates may be identical or different. Identical tilt angles are preferred. Preferred TN displays have pre-tilt angles between the longitudinal axis of the molecules at the surface of the outer plates and the outer plates of from 0° to 7°, preferably from 0.01° to 5°, in particular from 0.1 to 2°. In the STN displays, the pre-tilt angle is from 1° to 30°, preferably from 1° to 12° and in particular from 3° to 10°.

The twist angle of the TN mixture in the cell has a value of between 22.5° and 170°, preferably between 45° and 130° and in particular between 80° and 115°. The twist angle of the STN mixture in the cell from alignment layer to alignment layer has a value of between 100° and 600°, preferably between 170° and 300° and in particular between 180° and 270°.

The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner which is conventional per se. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, advantageously at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after thorough mixing.

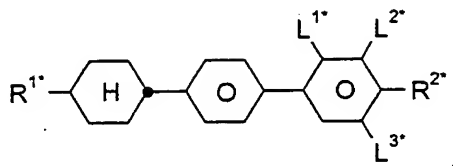
The dielectrics may also comprise further additives which are known to the person skilled in the art and are described in the literature. For example, 0-15% of pleochroic dyes, stabilisers, antioxidants, UV absorbers, etc., may be added. A particularly suitable UV absorber is a benzotriazole derivative, such as, for example, Tinuvin® from Ciba-Geigy.

In the present application and in the examples below, the structures of the liquid-crystal compounds are indicated by means of acronyms, the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals C_nH_{2n+1} and C_mH_{2m+1} are straight-chain alkyl radicals having n and m carbon atoms respectively. The alkenyl radicals have the trans-configuration. The coding in Table B is self-evident. In Table A, only the acronym for the parent structure is indicated. In individual cases, the acronym for the parent structure is followed, separated by a dash, by the code indicated in the table below for the substituents R^{1*}, R^{2*}, L^{1*}, L^{2*} and L^{3*}.

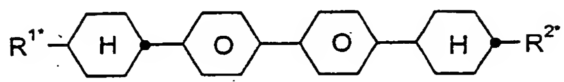
Code for R^{1*}, R^{2*}, L^{1*}, L^{2*}, L^{3*}	R^{1*}	R^{2*}	L^{1*}	L^{2*}	L^{3*}
nm	C_nH_{2n+1}	C_mH_{2m+1}	H	H	H
nOm	C_nH_{2n+1}	OC_mH_{2m+1}	H	H	H
nO.m	OC_nH_{2n+1}	C_mH_{2m+1}	H	H	H
n	C_nH_{2n+1}	CN	H	H	H
nN.F	C_nH_{2n+1}	CN	H	H	F
nN.F.F	C_nH_{2n+1}	CN	H	F	F
nF	C_nH_{2n+1}	F	H	H	H
nOF	OC_nH_{2n+1}	F	H	H	H
nF.F	C_nH_{2n+1}	F	H	H	F
nmF	C_nH_{2n+1}	C_mH_{2m+1}	F	H	H
nOCF$_3$	C_nH_{2n+1}	OCF_3	H	H	H
n-Vm	C_nH_{2n+1}	$-CH=CH-C_mH_{2m+1}$	H	H	H
nV-Vm	$C_nH_{2n+1}-CH=CH-$	$-CH=CH-C_mH_{2m+1}$	H	H	H

The TN and STN displays preferably contain liquid-crystalline mixtures composed of one or more compounds from Tables A and B.

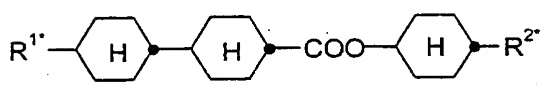
Table A: (L^{1*}, L^{2*}, L^{3*} = H or F)



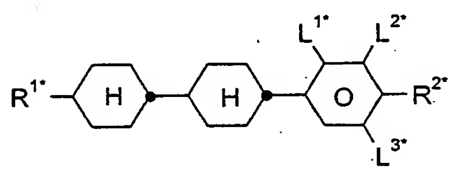
BCH



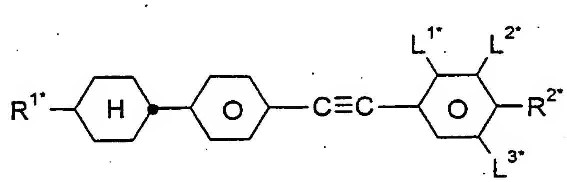
CBC



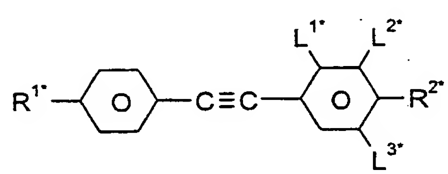
CH



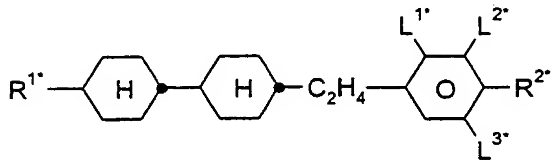
CCP



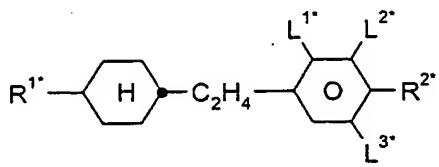
CPTP



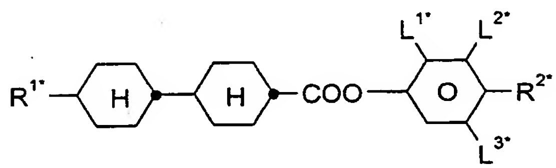
PTP



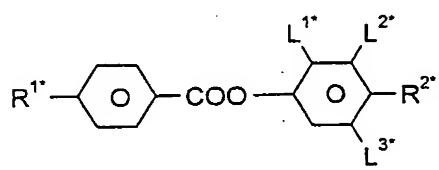
ECCP



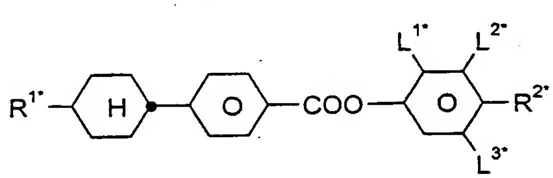
EPCH



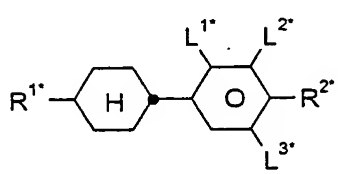
CP



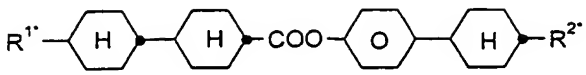
ME



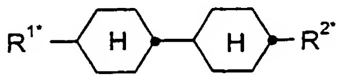
HP



PCH

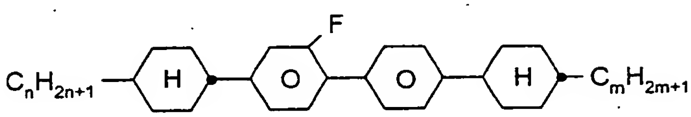


CCPC

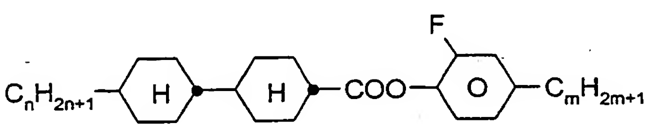


CCH

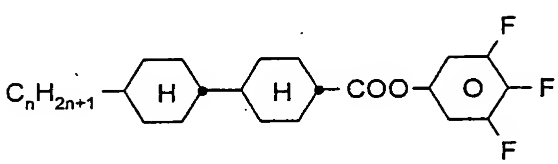
Table B:



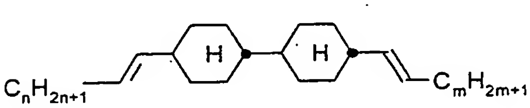
CBC-nmF



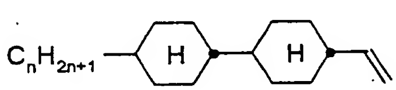
CP-nmF



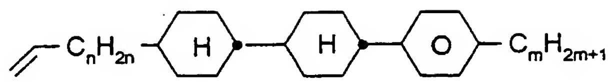
CCZU-n-F



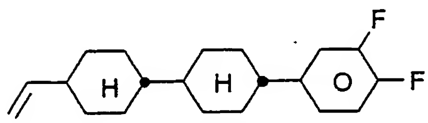
CC-nV-Vm



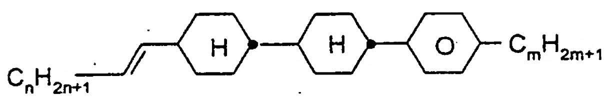
CC-n-V



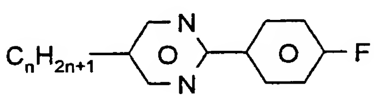
CCP-Vn-m



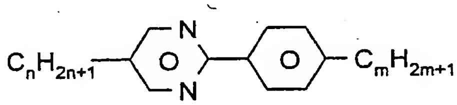
CCG-V-F



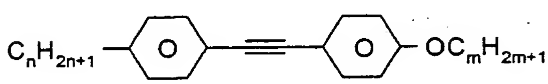
CCP-nV-m



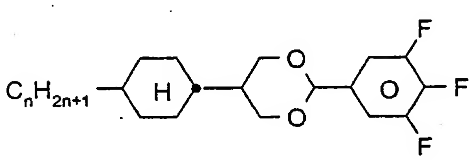
PYP-nF



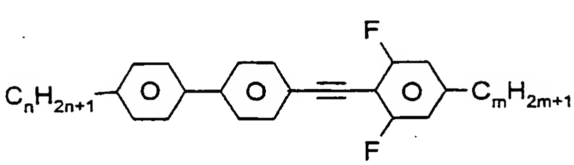
PYP-nm



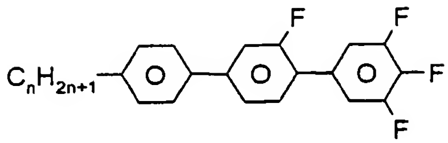
PTP-nOm



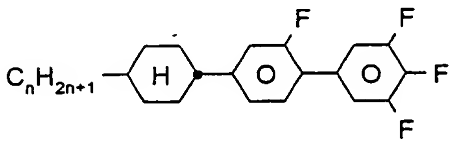
CDU-n-F



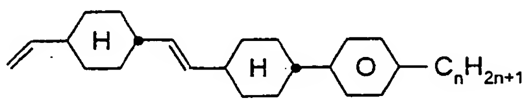
PPTUI-n-m



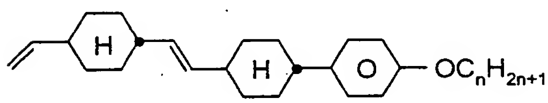
PGU-n-F



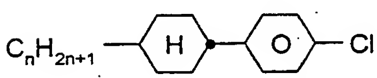
CGU-n-F



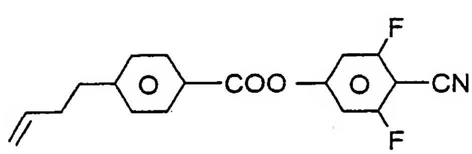
CVCP-V-n



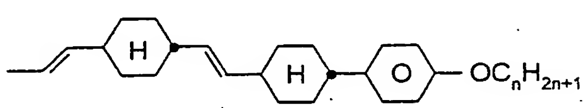
CVCP-V-On



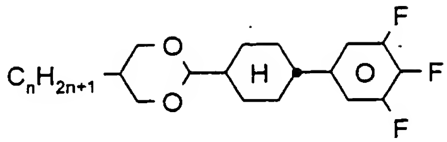
PCH-nCl



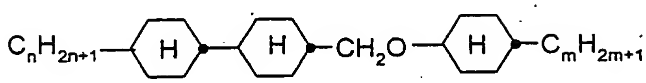
PZU-V2-N



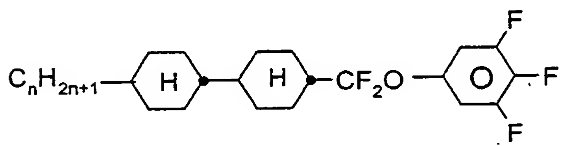
CVCP-1V-On



DCU-n-F



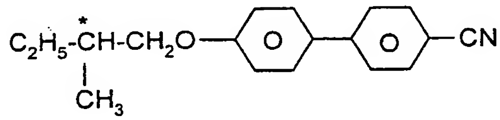
CCOC-n-m



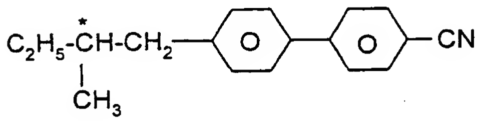
CCQU-n-F

Table C

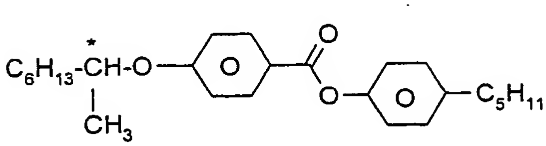
Table C shows dopants which are usually employed in the mixtures according to the invention.



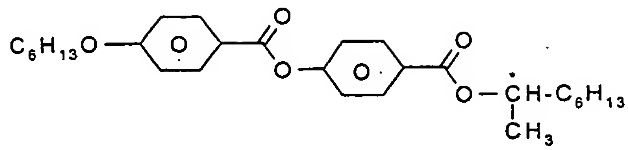
C 15



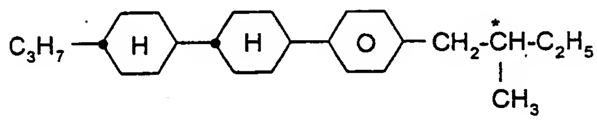
CB 15



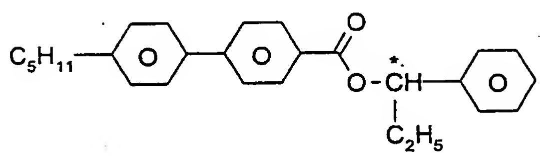
CM 21



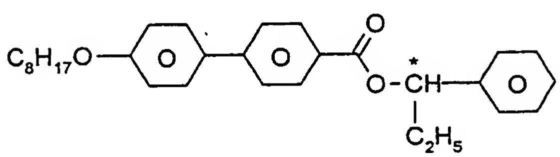
R/S-811



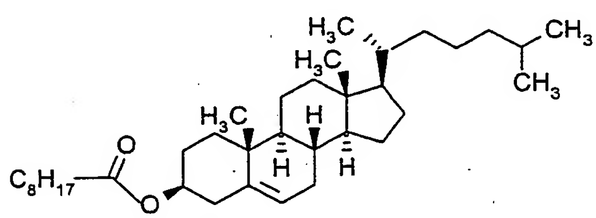
CM 44



CM 45



CM 47



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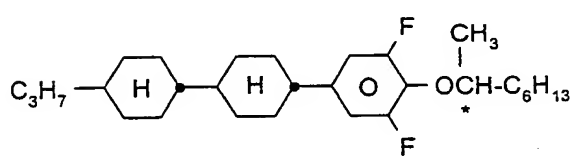
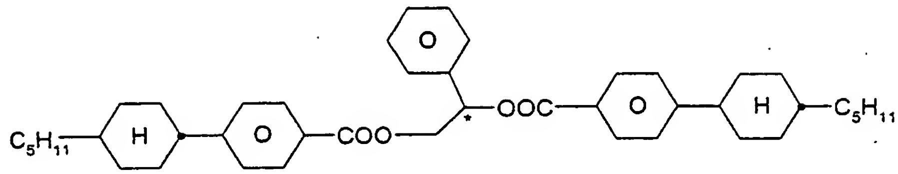
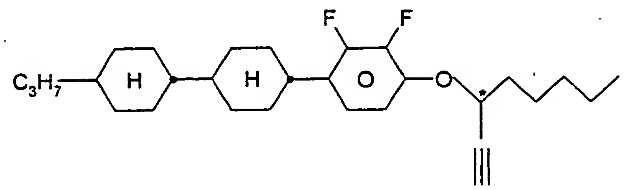


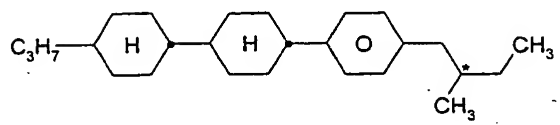
R/S-2011



R/S-1011



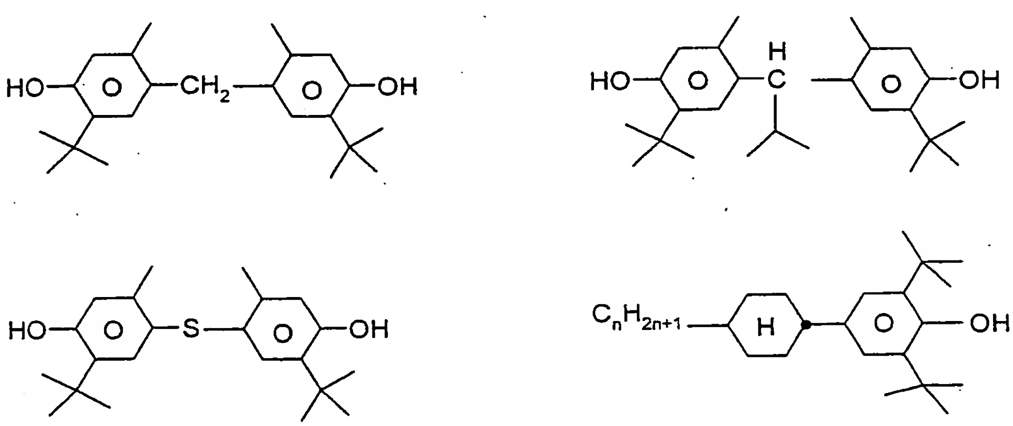
R/S-3011

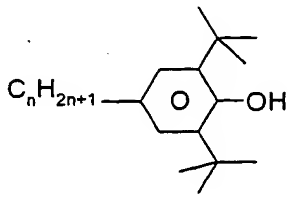


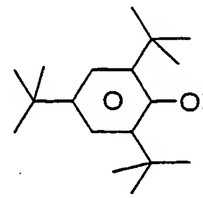
CM 44

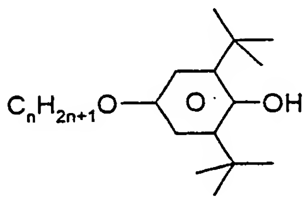
Table D

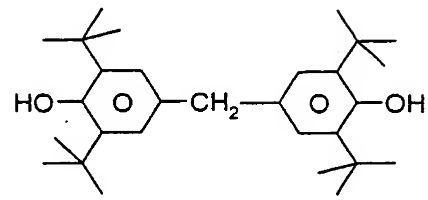
Stabilisers which can be added, for example, to the mixtures according to the invention are shown below.

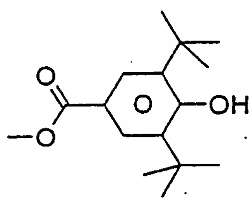


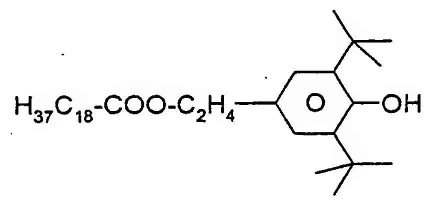


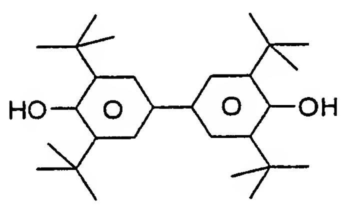


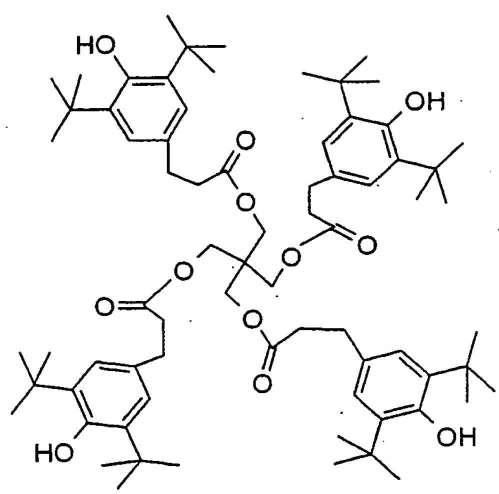


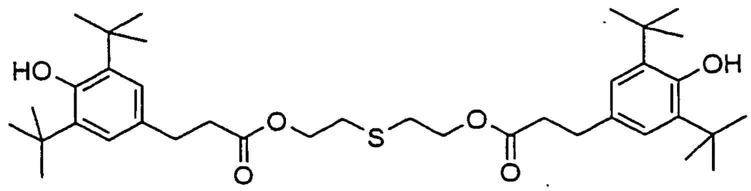


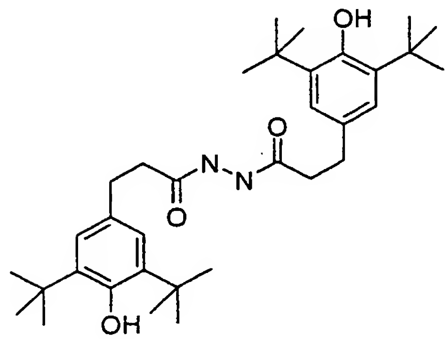


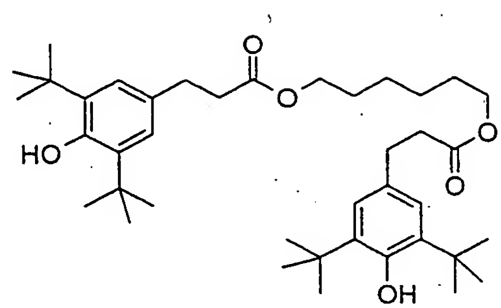


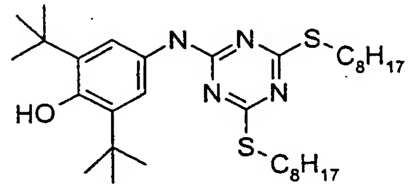


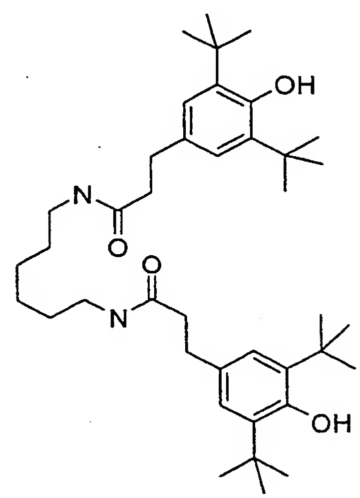


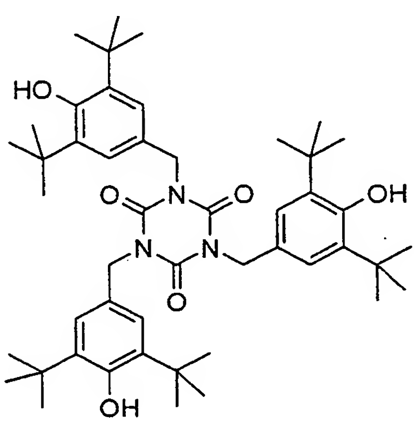


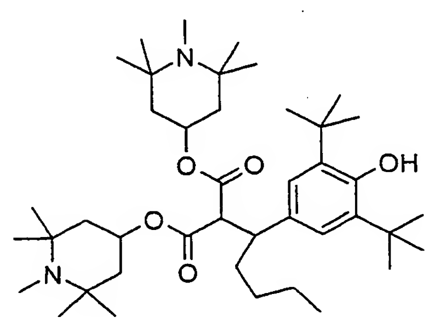


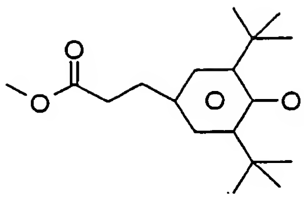


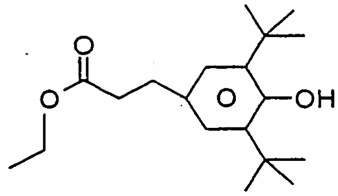


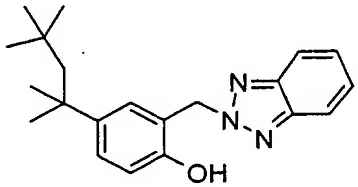


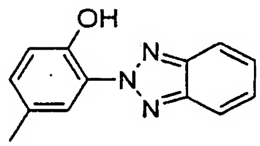


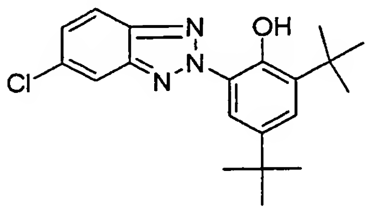


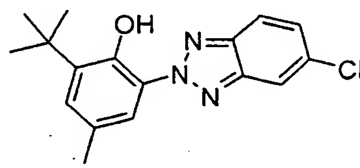

O
O
OH

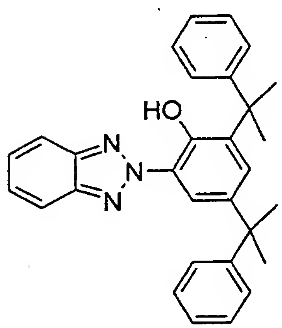

O
O
OH

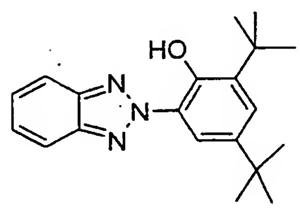

N
N
N
OH

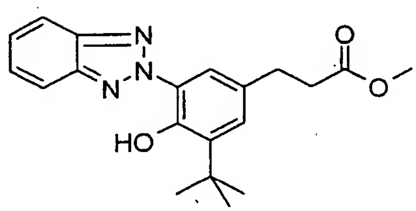

OH
N
N
N

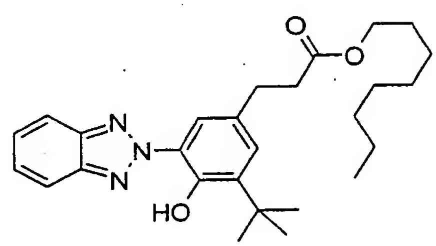

N
N
N
OH
Cl

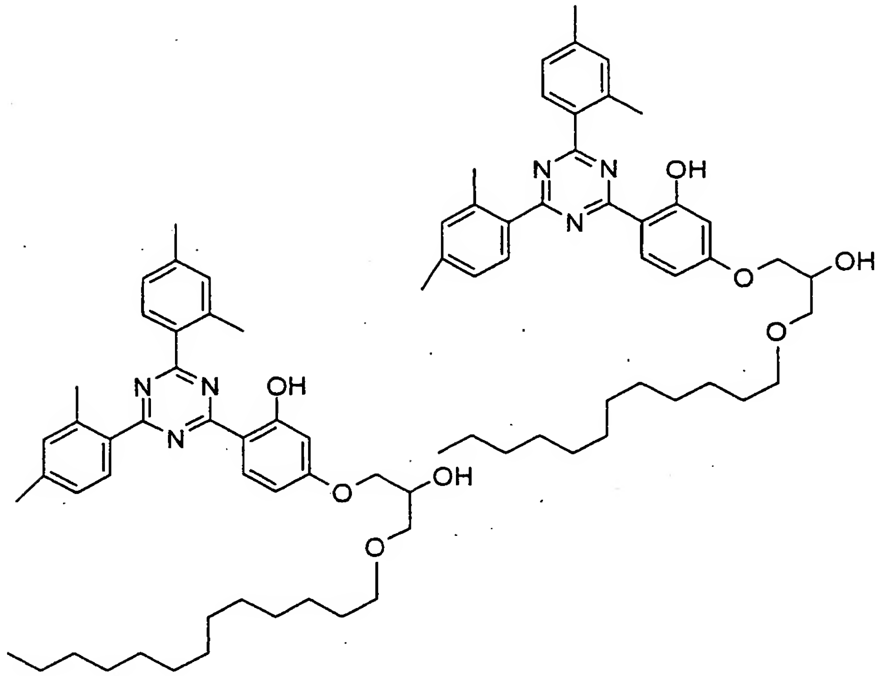

OH
N
N
N
Cl

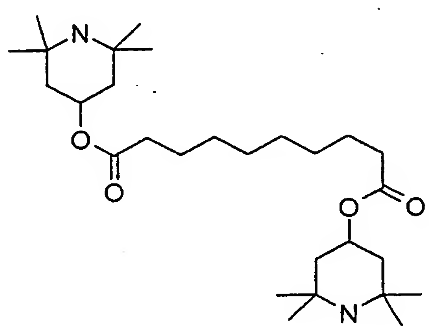

HO
N
N
N

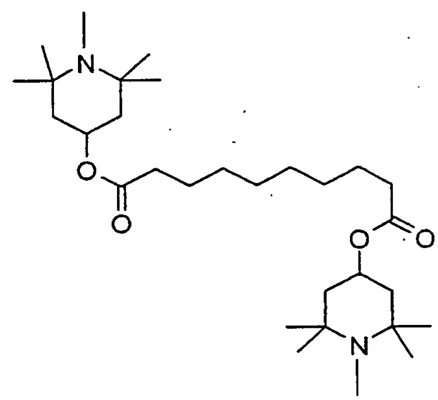

HO
N
N
N


N
N
N
O
O
HO


O
O
N
N
N
HO







The following examples are intended to illustrate the invention without representing a limitation. The following abbreviations are used:

cl.p.	clearing point (nematic-isotropic phase transition temperature)
S-N	smectic-nematic phase transition temperature
ν_{20}	flow viscosity (mm^2/s, unless stated otherwise, at 20°C)
Δn	optical anisotropy (589 nm, 20°C)
$\Delta\varepsilon$	dielectric anisotropy (1 kHz, 20°C)

γ_1	rotational viscosity (mPa · s at 20°C)
steep	characteristic-line steepness = V_{90}/V_{10}
V_{10}	threshold voltage = characteristic voltage at a relative contrast of 10%
V_{90}	characteristic voltage at a relative contrast of 90%
t_{ave}	$\frac{t_{on} + t_{off}}{2}$ (average response time)
t_{on}	time from switching on until 90% of the maximum contrast is reached
t_{off}	time from switching off until 10% of the maximum contrast is reached
mux	multiplex rate
t_{store}	low-temperature storage stability in hours (-20°C, -30°C, -40°C)

Above and below, all temperatures are given in °C. The percentages are per cent by weight. All values relate to 20°C, unless stated otherwise. The displays are addressed, unless stated otherwise, without multiplexing.

Example 1

ME2N.F	11.00%	Clearing point [°C]:	90.0
ME3N.F	11.00%	Δn [589.3 nm, 20°C]:	0.132
ME4N.F	14.00%	d · Δn [20°C, μm]:	0.85
ME5N.F	15.00%	Twist [°]:	240
CCQU-2-F	5.00%	V_{10} [V]:	0.95
CCQU-3-F	9.00%	V_{90}/V_{10}:	1.10
CCQU-5-F	4.00%		
CCG-V-F	10.00%		
CCP-V-1	7.00%		
CCPC-33	4.00%		
CCPC-34	5.00%		
CCPC-35	5.00%		

Example 2

PCH-3N.F.F	12.00%
ME2N.F	8.00%
ME3N.F	8.00%
ME4N.F	11.00%
ME5N.F	11.00%
HP-3N.F	4.00%
HP-4N.F	4.00%
HP-5N.F	4.00%
CCQU-2-F	5.00%
CCQU-3-F	10.00%
CCQU-5-F	5.00%
CCG-V-F	3.00%
CCPC-33	5.00%
CCPC-34	5.00%
CCPC-35	5.00%

Clearing point [°C]:	91.5
Δn [589.3 nm, 20°C]:	0.129
$d \cdot \Delta n$ [20°C, µm]:	0.85
Twist [°]:	240
V_{10} [V]:	0.89
V_{90}/V_{10}:	1.10

Example 3

PCH-3N.F.F	7.00%
ME2N.F	10.00%
ME3N.F	10.00%
ME4N.F	14.00%
ME5N.F	14.00%
HP-3N.F	6.00%
HP-4N.F	5.00%
HP-5N.F	5.00%
CCQU-2-F	5.00%
CCQU-3-F	9.00%
CCQU-5-F	5.00%
CCPC-33	5.00%
CCPC-34	5.00%

Clearing point [°C]:	84.0
Δn [589,3 nm, 20°C]:	0.141
$d \cdot \Delta n$ [20°C, µm]:	0.85
Twist [°]:	240
V_{10} [V]:	0.78
V_{90}/V_{10}:	1.13

Example 4

PCH-3N.F.F	7.00%	Clearing point [°C]:	62.5
ME2N.F	10.00%	Δn [589,3 nm, 20°C]:	0.141
ME3N.F	10.00%	d · Δn [20°C, μm]:	0.85
ME4N.F	14.00%	Twist [°]:	240
ME5N.F	14.00%	V_{10} [V]:	0.68
HP-3N.F	6.00%	V_{90}/V_{10}:	1.15
HP-4N.F	6.00%		
HP-5N.F	6.00%		
CCQU-2-F	5.00%		
CCQU-3-F	6.00%		
CCQU-5-F	5.00%		
CCPC-33	4.00%		
PZU-V2-N	7.00%		